The Constitution of the Alloys of Aluminium, Copper, and Zinc containing High Percentages of Zinc.

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[Plates 1 and 2.]

The following paper constitutes one of a series of researches on alloys, particularly on those containing aluminium, which is being carried out at the National Physical Laboratory, under the supervision and guidance of Dr. W. Rosenhain, F.R.S.

Introduction.

The ternary system copper-aluminium-zinc is of considerable interest, alike from the practical as from the theoretical point of view.

Portions of the ternary system have already been worked out. The copper-rich alloys have been investigated by Carpenter and Edwards.* The liquidus surface has been determined by these authors for the area CuBC (fig. 1), and the complete constitution for the area CuAC. As yet no constitutional diagram has been published for the aluminium-rich alloys of the series, but this forms the subject of one of the collateral researches being carried out in the National Physical Laboratory. The zinc corner (that part marked ZnDEF, fig. 1) is the subject of the present research.

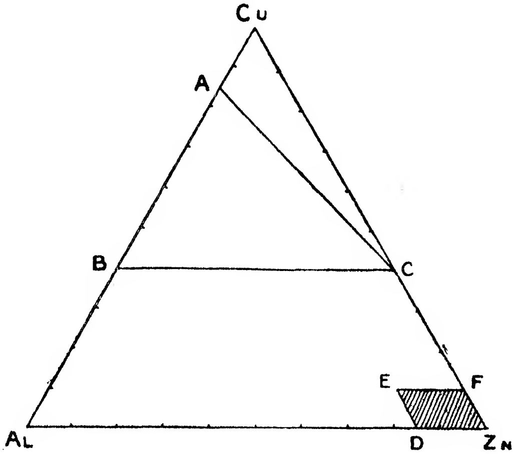

Fig. 1

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* H. C. H. Carpenter and C. A. Edwards, 'Internat. Zeits. f. Metallographie,' vol. 2, Part 4, p. 209 (1912).

The Binary Systems.

1.—*Copper-Aluminium.*—The system copper-aluminium has been investigated by Curry,* Gwyer,† Carpenter and Edwards,‡ and others.

The equilibrium diagram may be said to be fairly well established in the main, although there are certain details which require to be further investigated. As far as the present research is concerned, however, this diagram is of little importance.

2. *Aluminium-Zinc.*—The alloys of aluminium and zinc have been investigated by Shepherd,§ Rosenhain and Archbutt,|| and Bauer and Vogel.¶

3. *Copper-Zinc.*—That part of the copper-zinc diagram with which the present work is concerned has been investigated by Shepherd and Blough,** by Tafel,†† and others. Both diagrams are manifestly incomplete. It was considered advisable, therefore, as a preliminary to the main investigation, to redetermine that part of the equilibrium diagram of copper-zinc alloys containing from 90 per cent. to 100 per cent. of zinc.

Before referring to the results obtained in the present research, it will be advisable to describe in some detail the methods and apparatus employed in the investigation. The methods were :—

1. Thermal curves.
2. Microscopic examination of annealed and quenched specimens.
3. Electrical conductivity measurements.

1. *Thermal Curves.*—The thermal curves were taken in a "gradient" furnace of the type described by Rosenhain in his paper on "Some Appliances for Metallographic Research."‡‡ As this particular furnace was not required for high temperature work, the tube carrying the winding was made of iron, in order to obtain a more gradual temperature gradient than was possible by the use of a fireclay tube. The specimens employed weighed about 50 grm. and were carried in a small clay pot, which was made with a tube of the same material passing in from one side. The pot was carried in an iron cylinder, which was hung from the winding gear by three "Nichrome" wires,

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* H. E. Curry, 'Jnl. Phys. Chem.,' vol. 11, p. 425 (1907).

† A. G. C. Gwyer, 'Zeits. f. Anorg. Chem.,' vol. 57, p. 113 (1908).

‡ H. C. H. Carpenter and C. A. Edwards, 'Proc. Inst. Mech. Eng.,' vol. 57 (1907).

§ E. S. Shepherd, 'Jnl. Phys. Chem.,' vol. 9, p. 504 (1905).

|| W. Rosenhain and S. L. Archbutt, 'Phil. Trans.,' A, vol. 211, p. 315 (1911).

¶ O. Bauer and O. Vogel, 'Internat. Zeits. f. Metallographie,' vol. 8, p. 107 (1916).

** E. S. Shepherd and Blough, 'Jnl. Phys. Chem.,' 1904.

†† V. E. Tafel, 'Metallurgie,' vol. 5, p. 375 (1908).

‡‡ W. Rosenhain, "Some Appliances for Metallographic Research," 'Journ. Inst. of Metals,' vol. 13, No. 1, p. 160 (1915).

passing through holes in a ring, which kept them in place. The suspending wire and the two thermocouple wires passed through a silica tube, and the junction of the couple was inserted into the tube in the side of the crucible, the orifice of which was then packed with asbestos wool. This tube was made very thin at the end, so as to reduce the thermal lag to a minimum. The couple employed was an iron-constantan one, which was carefully calibrated before and after the curves were taken, the melting points of tin, lead, and zinc being used for the purpose. The two sets of calibrations show only negligible differences.

The specimen was raised and lowered in the furnace by means of a weight, the speed of the motion being controlled by the movement of a piston in a cylinder of oil. Readings were taken every 2° C., and the rate of heating or cooling was of the order of 5° C. per minute.

The curves were recorded on the Rosenhain plotting chronograph,* the paper being reversed on the drum between heating and cooling, so that the temperature ordinates were the same for the two curves.

2. *Microscopic Examination.*—The microscopic examination calls for no special comment. The specimens were annealed and quenched before examination, except in special cases where very slowly cooled or chill cast alloys were examined. When it was necessary to anneal for very long periods, this was carried out in a Haughton-Hanson thermostat,† the specimens being tied together and to the thermo-couple with a thin "Nichrome" wire. In order to avoid the risk of contamination, the specimens were insulated from the wire and from each other by a thin strip of asbestos paper. When the annealings were completed, the specimens were rapidly withdrawn from the furnace by means of the thermo-couple and plunged into a basin of cold water. In these cases where rapidity of quenching was of more importance than prolonged annealing, *e.g.*, in the case of the determination of the solidus, a Rosenhain quenching furnace was used. As, however, it has been shown by Thorneycroft and Turner,‡ that, *in vacuo*, copper-zinc alloys containing about 10 per cent. of copper lose from 20 per cent. to 25 per cent. of their zinc at temperatures similar to those at which the annealings were carried out, it was not considered advisable to use a vacuum in order to obtain the desired inrush of quenching water. Instead of this, a rapid stream of water from a tap was injected into the furnace, and this washed the

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* W. Rosenhain, *loc. cit.*

† J. L. Haughton and D. Hanson, "A Thermostat for Moderate and High Temperatures," 'Journ. Inst. of Metals,' vol. 14, p. 145 (1915). "Further Notes on a High Temperature Thermostat," *ibid.*, vol. 18 (1917).

‡ W. E. Thorneycroft and T. Turner, "Behaviour of Copper-Zinc Alloys when Heated in a Vacuum," *ibid.*, vol. 12, p. 214 (1914).

specimen into a vessel of water placed at the end of the furnace. A very rapid quench was obtained by this means.

In a few cases it was necessary to cool the alloys slowly, from a point above the liquidus, to a temperature intermediate between this line and the solidus. In order to do this, the specimens were placed in a small glass crucible, the thermo-couple being inserted into a narrow glass tube sealed into it. Fragments of the alloys were placed in this crucible, which was then hung, by means of very thin copper wire, inside a vertical tube furnace, mounted over a beaker of water. The furnace was run in parallel with a thermostat, fitted with the slow cooling device described in the paper referred to above, and the desired rate of cooling was obtained. When the specimen had reached the temperature at which it was to be quenched, the supporting wire was fused electrically, and the pot and specimen fell into the water.

It was found possible, in many cases, to etch the alloys by exposing them to the atmosphere, but this was not a suitable method for detecting the first appearance of the ϵ constituent. Numerous reagents were tried, and a very satisfactory one was found to be that of Tinoféef.* This reagent was suitable for all the alloys investigated, and was almost invariably used. In a few cases, however, specimens were given a preliminary air etch, and then treated with Tinoféef's reagent, while in other cases electrolytic etching with 4 per cent. hydrochloric acid in water was used.

Towards the end of the research, it was found that, to obtain good contrast between the three constituents, the most satisfactory method was to use an electrolytic etch in a solution consisting of twenty drops of concentrated hydrochloric acid in 50 c.c. of alcohol.

3. *Electrical Conductivity.*—The electrical conductivity of the alloys was determined by measuring the drop of potential along a measured length of the specimen, through which a constant current was maintained. The apparatus employed, and the method of carrying out the tests, have been described by one of the authors in a paper read before the Faraday Society.†

The Equilibrium Prism.

It is well known that the equilibrium conditions of alloys of three metals can be represented by a triangular prism. Sections through such a prism, taken parallel to one of the sides, represent a series of alloys in which one of the metals is present in constant quantity, and the other two are variable, while sections parallel to the base represent the entire series at a definite temperature.

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* Tinoféef's reagent is made by dissolving 6 grm. of chromium oxide in 94 grm. of nitric acid. A few drops of this solution are then added to 50 c.c. of water.

† J. L. Haughton, "The Measurement of Electrical Conductivity in Metals and Alloys at High Temperatures," 'Trans. Faraday Society,' vol. 16 (1920).

Figs. 2–9 represent a series of such sections parallel to the aluminium-zinc side of the prism, the copper contents being 0, 1, 2, 3, 4, 5, 7, and 9 per cent. respectively. Fig. 2 is copied from Rosenhain and Archbutt's diagram, referred to above. Figs. 10–17 are sections parallel to the copper-zinc side of the prism, the aluminium contents being 0, 2, 4, 6, 8, 10, 12, and 15 per cent. Fig. 18 is a contour plan of the liquidus surface, while figs. 19, 20 and 21 are sections cut through the complete series at temperatures of 400° C., 300° C., and 200° C.

From such a series of cross-sections, a temperature-concentration model can be constructed.

At Dr. Rosenhain's suggestion, the authors constructed a wire model,* and figs. 22, 23, and 24 have been drawn from this model, the various planes being cross-hatched, so as to represent progressive cooling of the alloys. These figures, together with the various sections, are explained below, under their proper headings.

The liquidus curves of the various sections have been determined solely from the thermal curves, except in one case, where the results obtained from the temperature-conductivity curve were also used. In some cases, the indications on the heating curves of the completion of fusion were so incomplete that it was considered advisable to neglect them and use the data from cooling curves only.

The various solidus curves were obtained from the thermal analysis when the solidus happened to be an eutectic or a transformation, otherwise they were obtained from the examination of quenched specimens, and in one case confirmed by electrical conductivity measurements. Reactions occurring in the solid were detected by the thermal curves and confirmed by electrical conductivity methods, and by microscopic examination of annealed and quenched specimens.

Limits of solubility were determined by microscopic examination of specimens which were quenched after long annealings in the thermostat furnace.

Nomenclature.—In order to avoid referring to the composition of the alloys in detail, a nomenclature has been adopted, in which numerals representing the approximate copper and aluminium contents are separated by the letter Z, which represents zinc. Thus, 5Z7 represents an alloy whose composition is approximately:—

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* W. Rosenhain, "Model representing Ternary Alloys," 'Journ. Inst. of Metals,' vol. 23, p. 247 (1920).

	Per cent.
Cu	5
Zn	88
Al	7

As the alloys were very carefully made up from previously made and

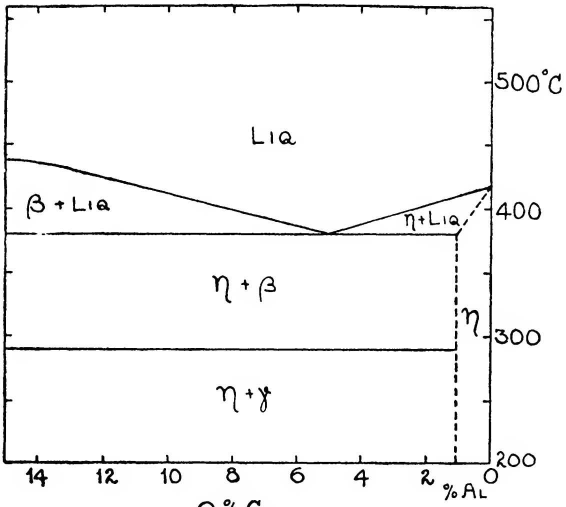

Fig. 2.

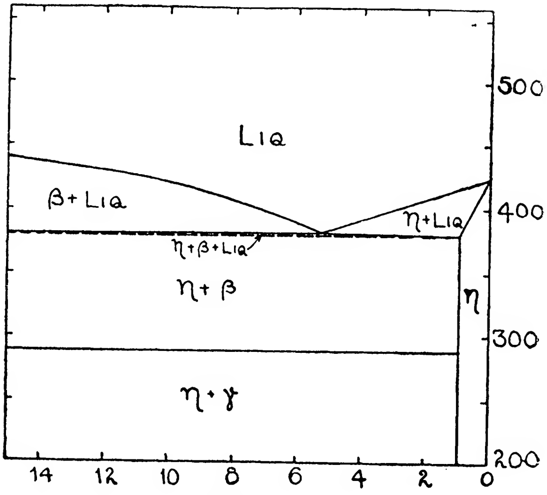

Fig. 3.

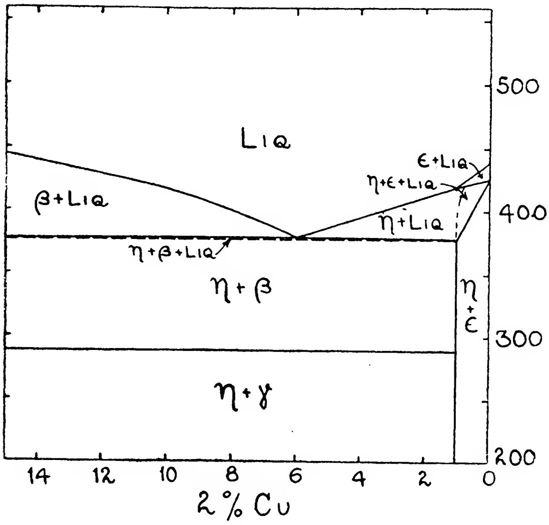

Fig. 4.

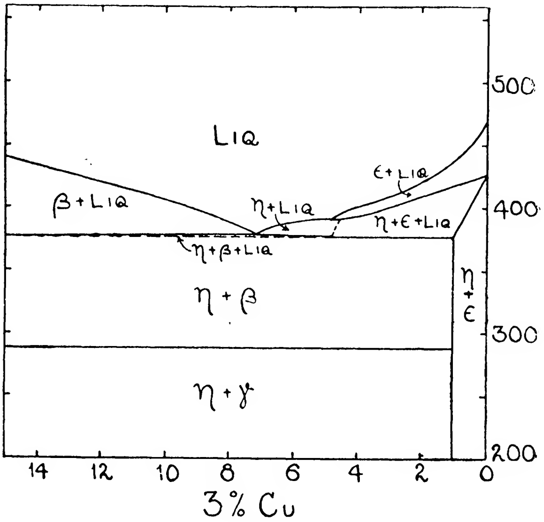

Fig. 5.

analysed "basis" alloys (50 per cent. Al, 50 per cent. Cu, and 90 per cent. Zn, 10 per cent. Cu respectively), the actual composition varies but slightly from that indicated by the nomenclature.

The Copper-Zinc Series.—As has been indicated earlier in this paper, the first step to be taken was the redetermination of the constitution of the copper-zinc alloys containing between 90 and 100 per cent. of zinc. The

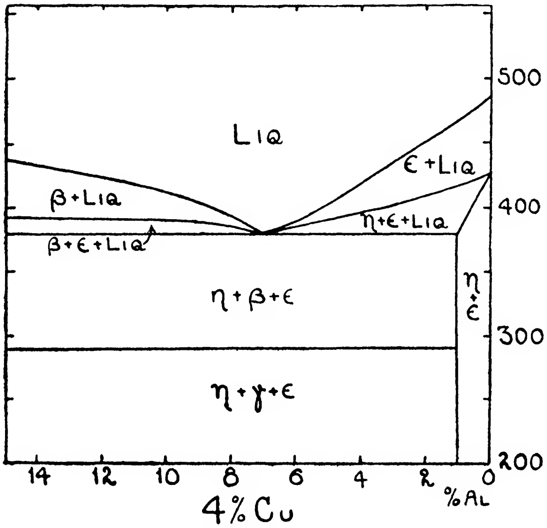

Fig. 6.

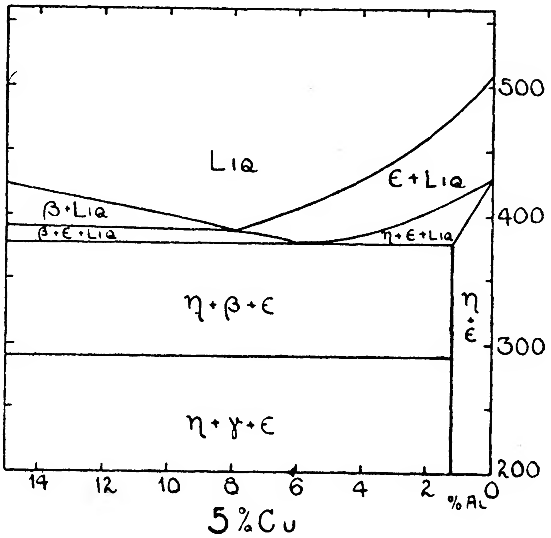

Fig. 7.

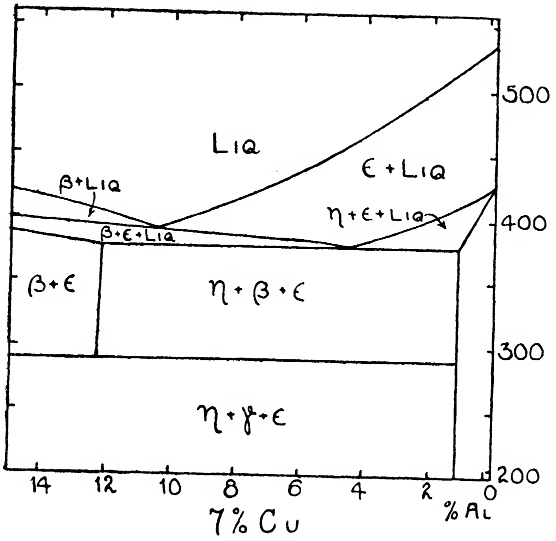

Fig. 8.

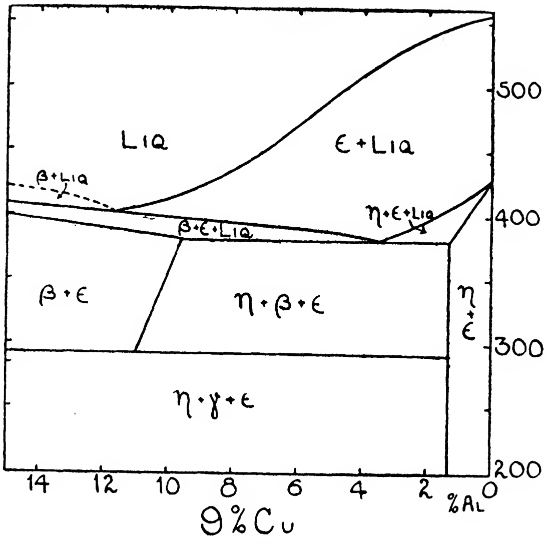

Fig. 9.

result obtained by the authors is given in fig. 10. The liquidus agrees well with that of Tafel, while the temperature of the reaction

$$\epsilon + \text{liquid} = \eta$$

is found to be 426° C. This, again, is in excellent agreement with Tafel, who gives a temperature of about 425° C. for the reaction as compared with 419° C., which is the temperature indicated by Shepherd and Blough.

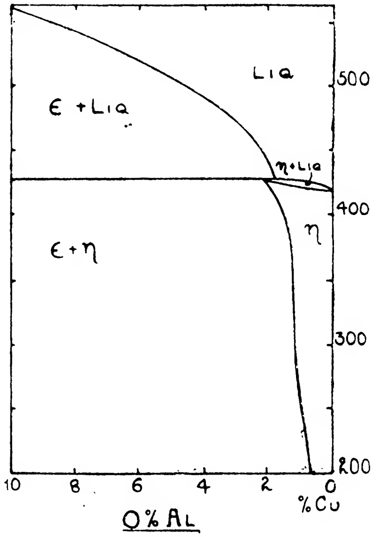

Fig. 10.

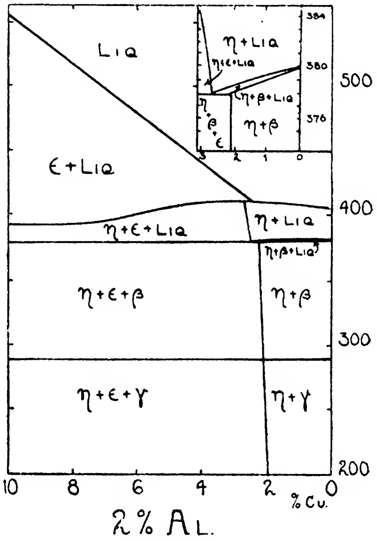

Fig. 11.

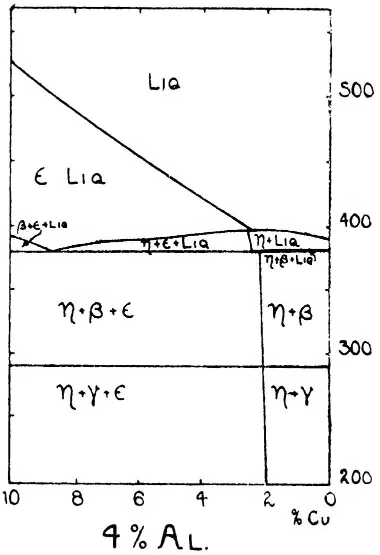

Fig. 12.

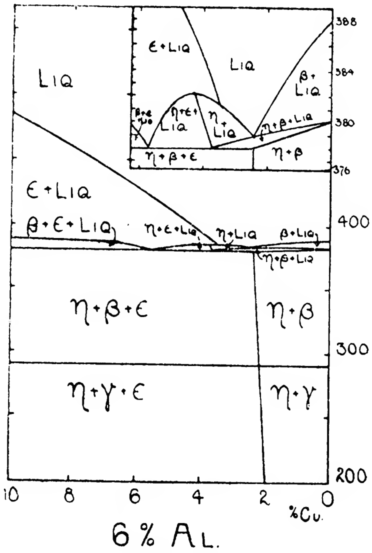

Fig. 13.

The determination of the solidus between the limits of 0 and 2 per cent. of copper was a matter of considerable difficulty, as the maximum range between the liquidus and solidus was found to be 5° C. By quenching the specimens at temperatures rising by about 1° C. at a time, and examining them under the microscope, it was possible to detect the first appearance of fusion spots, *i.e.*, places which were molten at the moment of quenching. The alloys which were examined in this way were ¼Z0, 1Z0, 1½Z0, and 2Z0.* By this means it was found possible to determine the solidus with an

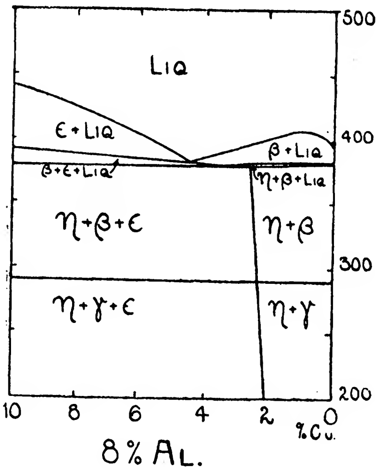

Fig. 14.

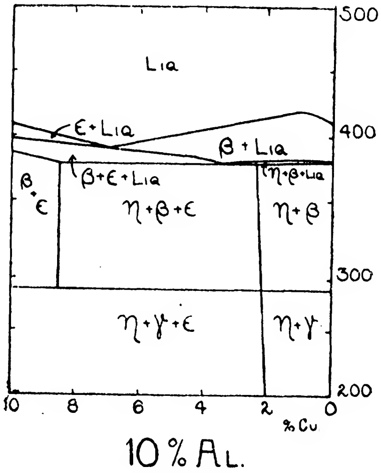

Fig. 15.

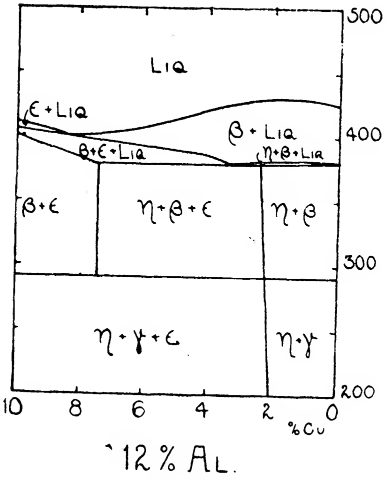

Fig. 16.

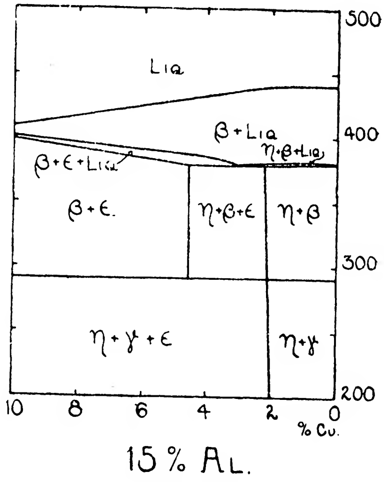

Fig. 17.

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* Analysis showed that the composition of these alloys was 0·26 per cent., 0·95 per cent., 1·30 per cent. and 1·80 per cent. of copper respectively.

error probably not greater than ± 1° C. Confirmation of this was found from a temperature-electrical conductivity curve taken of alloy 1Z0, which is reproduced in A, fig. 25. The more or less horizontal part of this curve

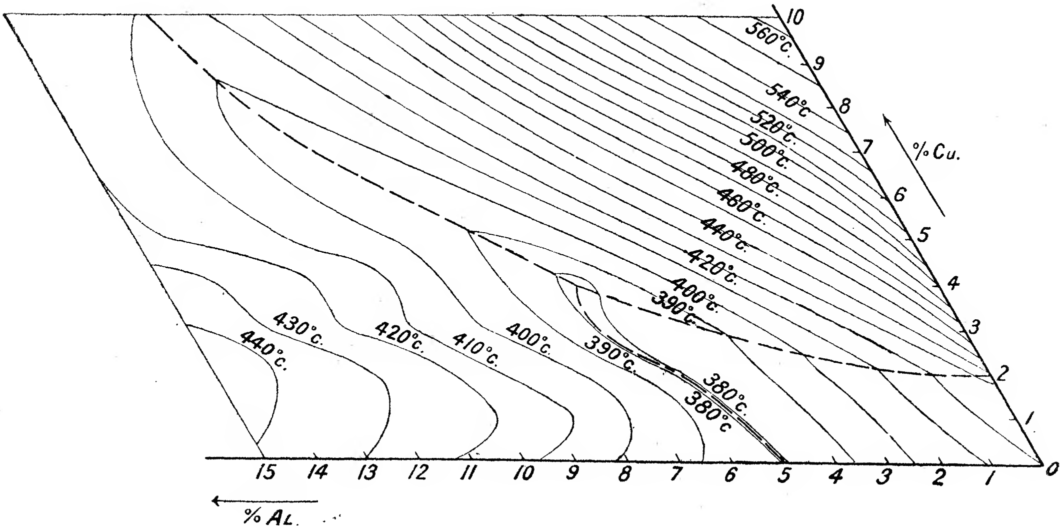

FIG. 18.

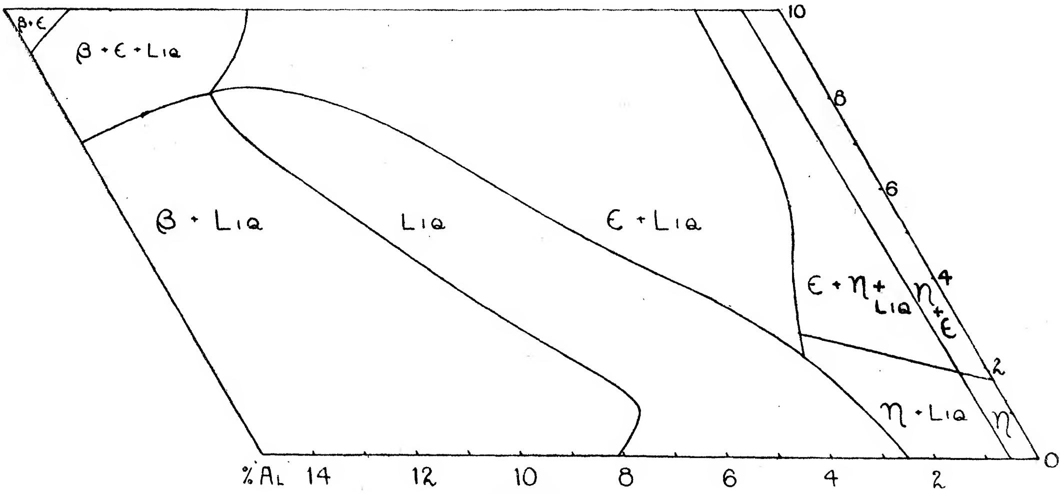

FIG. 19.

represents the resistance of the material during the change from the liquid to the solid state, and will be seen to have a range of about 5° C. For purposes of comparison, the curve for pure zinc is given as B in fig. 25.

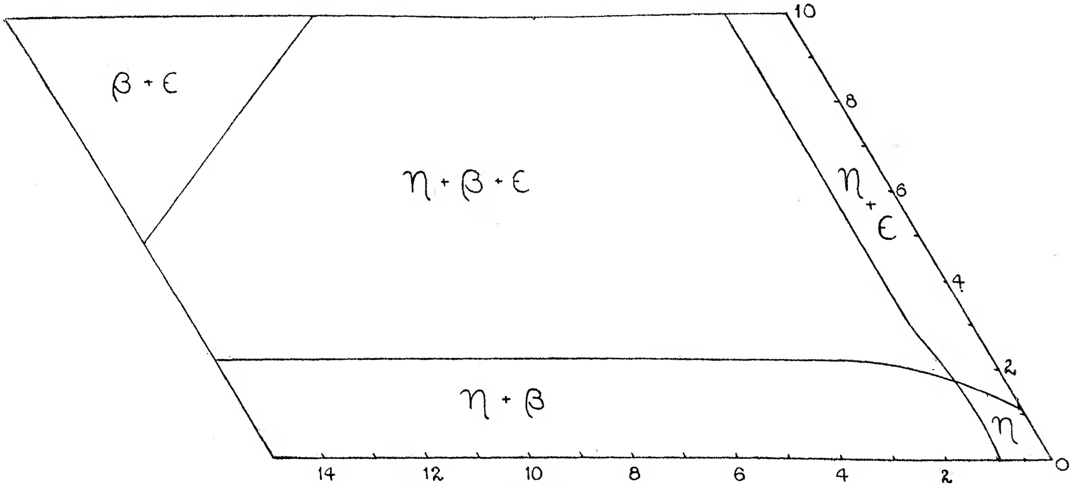

FIG. 20.

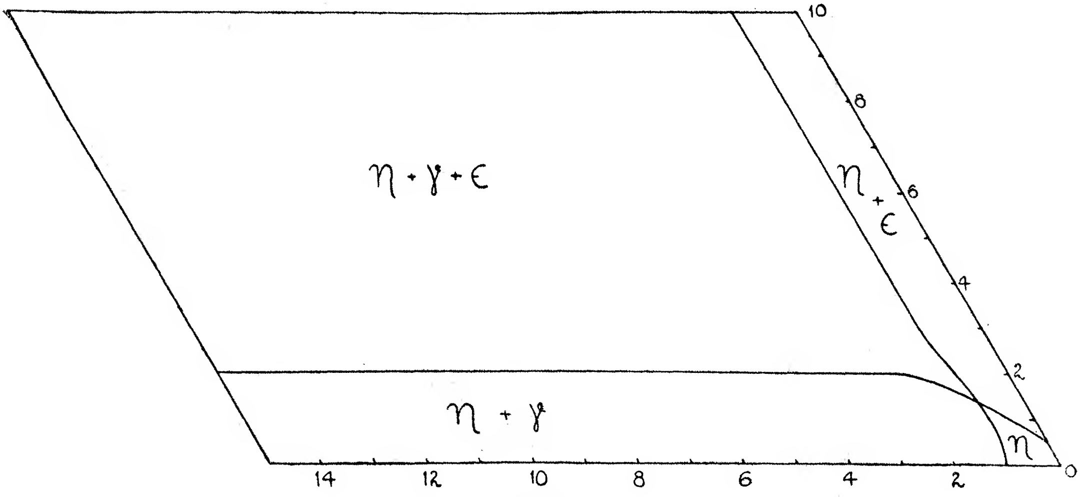

FIG. 21.

The Ternary Diagram.

The results obtained in the investigation of the ternary system are shown in figs. 3 to 17.* The case of the alloys containing 1 per cent. copper is very simple, and the same may be said of those having a copper-content of 2 per cent., with the exception of a small corner near the pure copper-zinc end (figs. 3

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* The α constituent of the Al-zinc series, and the η constituent of the copper-zinc series are isomorphous. In order to avoid confusion, the term α has been omitted altogether, and the homogeneous zinc rich solid solution of either copper or aluminium or both, has been called η in this paper.

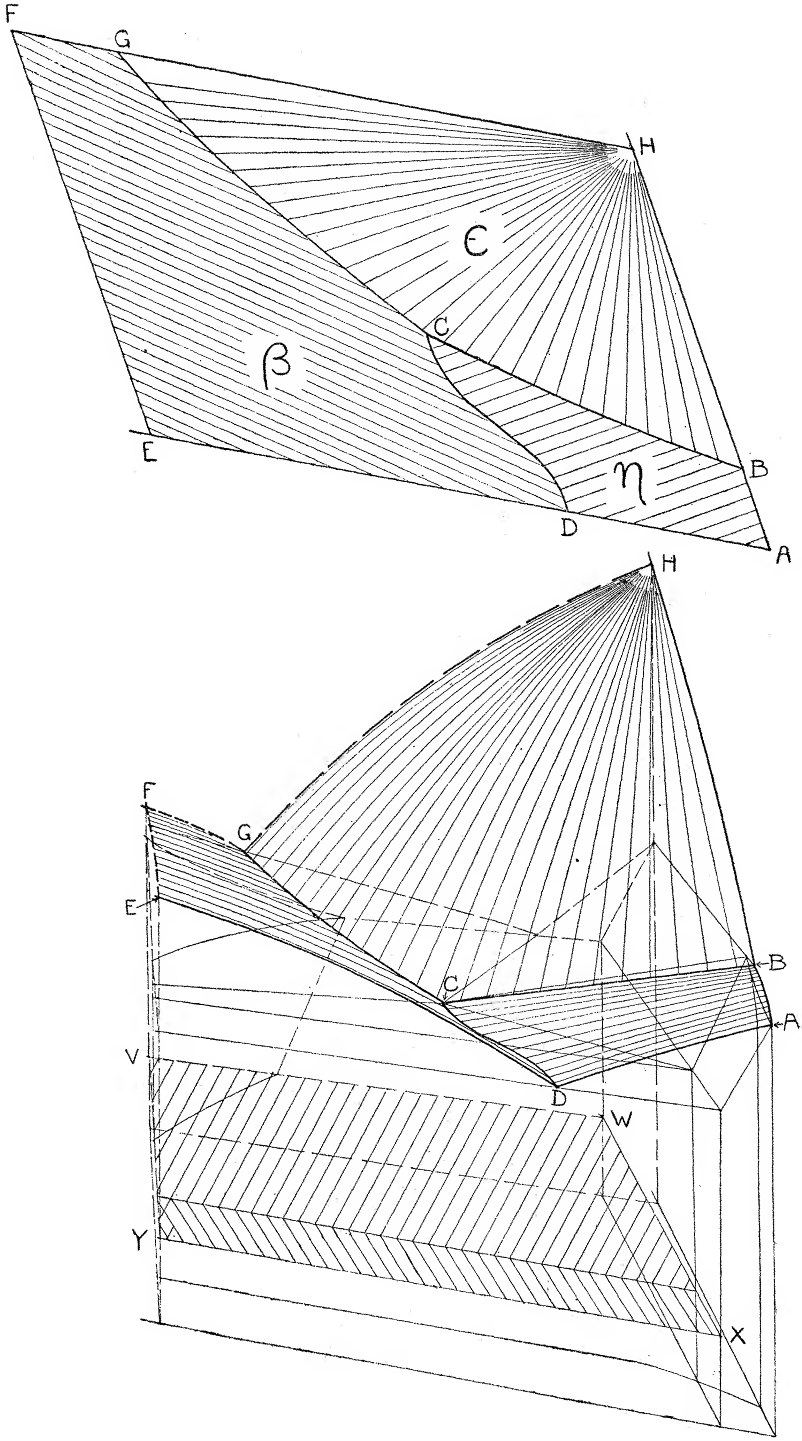


Fig. 22.

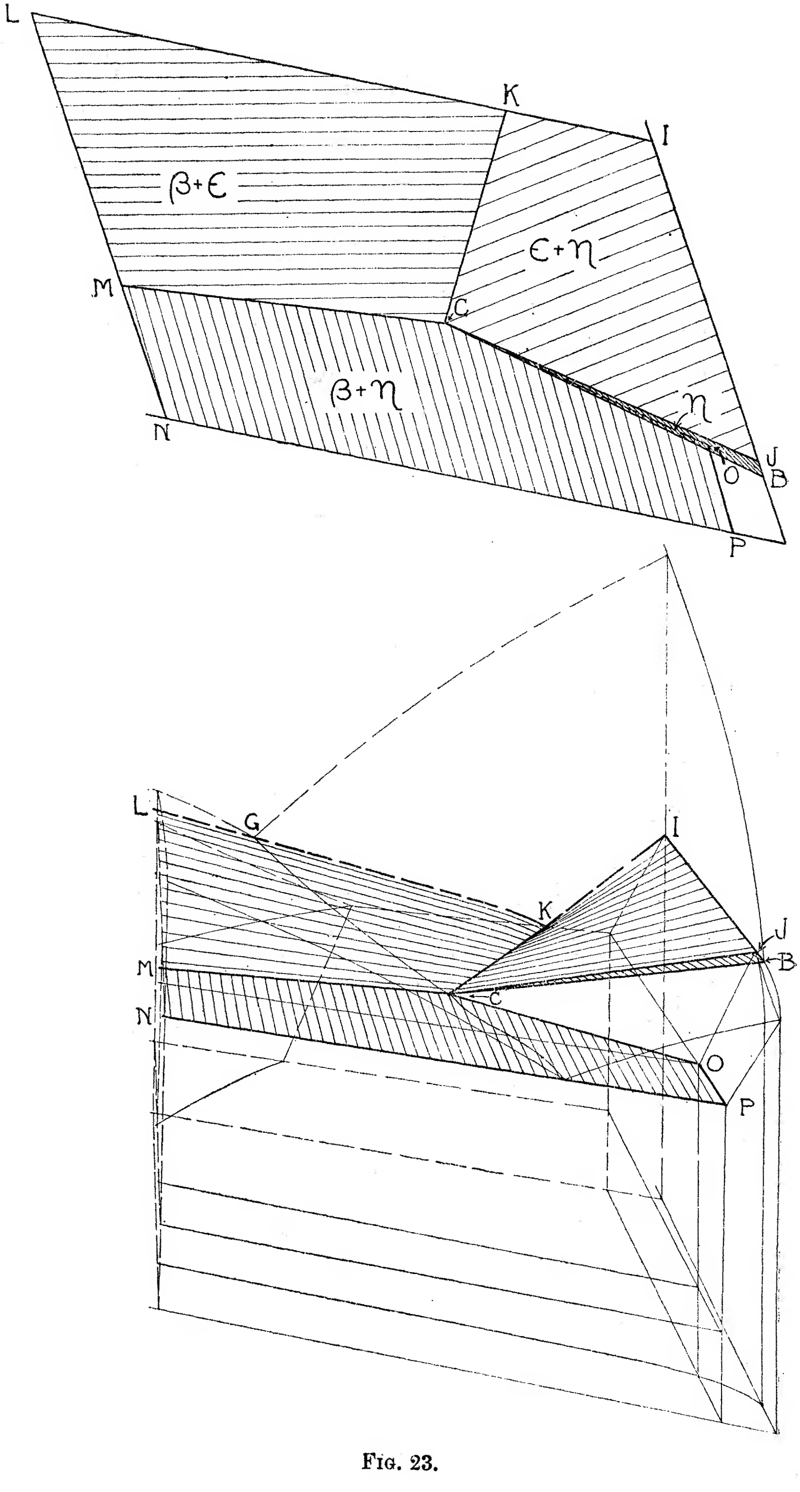


Fig. 23.

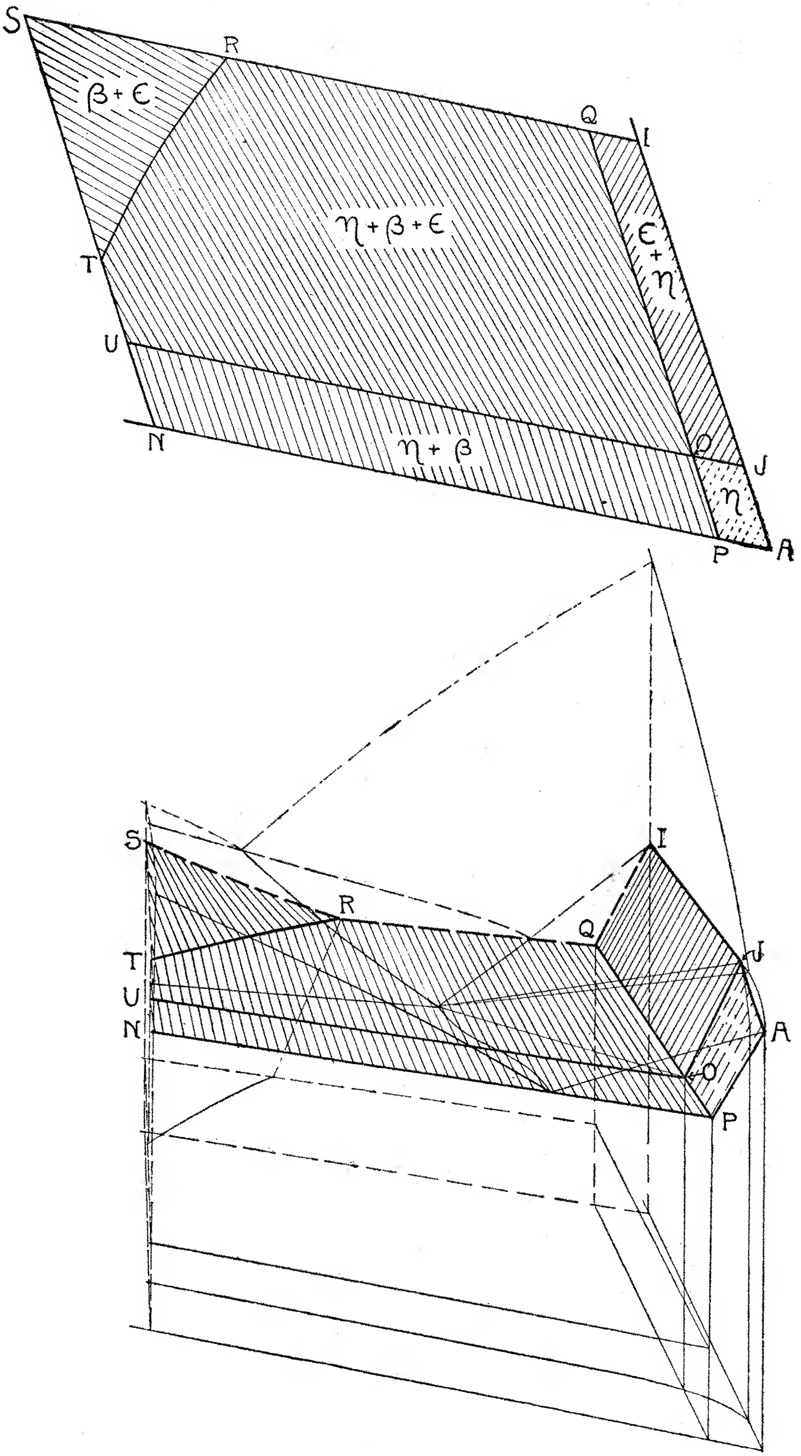


FIG. 24.

and 4). These diagrams, with the exception just referred to are, practically, repetitions of the aluminium-zinc diagram as far as they have been investigated (*i.e.*, up to 15 per cent. Al). The eutectic of the series, however, being a binary complex in a ternary system, cannot solidify at a constant temperature, but the solidification must take place over a range which must be lower than the temperature at which the pure eutectic forms. The range appears, however, to be so small as to be beyond the limits which can be detected by the pyrometer, and one of the lines has therefore been shown dotted on the diagram. The evidence for the lowering of the temperature seems somewhat more marked, though it is still very slight, amounting to about 2° C. between the temperature of solidification of the pure binary eutectic and that of the ternary eutectic which occurs in the alloys containing 3 per cent. of copper and over.

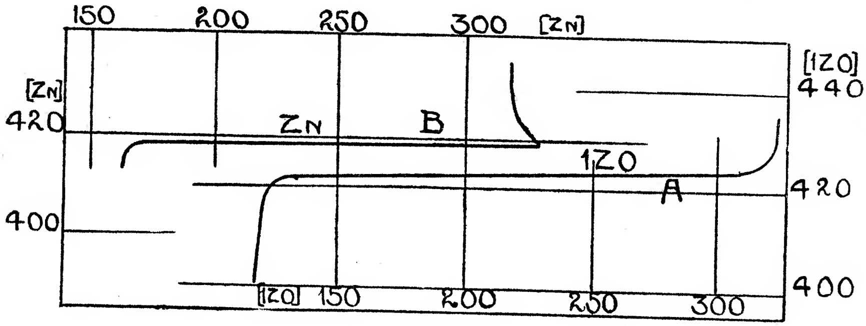


Fig. 25.

The diagrams of the series containing 4, 5, 7, and 9 per cent. of copper (figs. 10 to 13) are of the same kind, the only difference being the composition and temperature at which the various reactions occur. A consideration of any one of these sections will, therefore, be sufficient to enable the other three to be understood, and for this purpose the alloys containing 7 per cent. of copper have been selected, as in this series the various reactions are all well developed.

On cooling an alloy containing 7 per cent. of copper and 0·5 per cent. of aluminium, the first substance to separate from the liquid is the copper-zinc solid solution ϵ (containing a small amount of aluminium in solution, as is shown by the depression of its freezing point). This separation commences at a temperature of 523° C. and continues until 417° C. is reached, when the solid reacts with the liquid according to the equation

$$\epsilon + \text{liquid} = \eta.$$

In the pure copper-zinc series this reaction takes place at a constant temperature, but in the ternary system, not only is the temperature depressed, but the reaction continues over a range: in the case of the alloy under consideration, until 390° C. is reached, when the whole of the liquid is used up, and ϵ and η are left. This is shown in fig. 26 (Plate 1). In this and in figs. 27, 28, and 29 are shown photomicrographs of alloys which have been cooled slowly from a temperature considerably above the liquidus down to 350° C.

Considering next the alloy with the same copper-content, but with 2 per cent. of aluminium, we find as before, solidification commences by the separation of the ϵ crystals from the liquid, the temperature in this case being 495° C. At 398° C. the reaction giving rise to η commences, continuing with falling temperature until 378° C. is reached, when the remaining liquid solidifies at a constant temperature in the form of a ternary eutectic (fig. 27). The nature and manner of formation of this eutectic will be discussed later.

An alloy containing 8 per cent. of aluminium (7Z8) behaves very differently. As in the case of 7Z½ and 7Z2 the first constituent to separate is ϵ, the separation commencing at 415° C. This, however, never reacts with the liquid to form η, but when the temperature has fallen to 388° C. a binary complex of ϵ with the β solution of the aluminium-zinc series (Al_2Zn_3) commences to separate from the liquid. This separation proceeds until the temperature of 378° C. is reached, when the ternary eutectic solidifies. The alloy, when solid, will therefore show primary separation of ϵ and sub-primary or secondary separation of the β-complex in a matrix of the ternary eutectic (fig. 28).

Referring next to the alloy containing 10·5 per cent. of aluminium (7Z10½). Here the first solid to separate is no longer ϵ but the $\beta-\epsilon$ complex referred to above. This separation commences at 392° C. and continues until the ternary eutectic solidifies. The solid alloy will therefore consist of primary spherulitic dendrites of the complex embedded in the ternary eutectic (fig. 29).

The first separation from the alloy 7Z12 takes place at a temperature of 402° C., and consists of β-crystals. These continue to separate over a range of 8° C., when the complex begins to solidify, and at 378° C. as before, the remaining liquid freezes as the ternary eutectic. The just solid alloy will, therefore, consist of primary β and secondary $\beta-\epsilon$ complex with a certain amount of ternary eutectic (see fig. 30). Finally, the alloy 7Z15 commences to solidify in a similar manner at 420° C., and at 400° C. the $\beta-\epsilon$ complex begins to separate, this separation continuing until the temperature of 390° C. is reached, when the whole alloy is solid (fig. 31). It will be seen that in this case there will be no ternary eutectic present. Figs. 30 and 31 are photographs of alloys which have been chill cast and annealed for long periods to remove the last traces of metastable ternary eutectic. This accounts for the difference in the scale of the structure compared with that of figs. 27, 28 and 29.

The nature of the $\beta-\epsilon$ complex is particularly interesting. It is the only case with which the authors are acquainted where a binary complex is formed in a ternary system without any corresponding eutectic existing in any of the binary systems. In this case, one of the constituents of the complex belongs essentially to one of the binary systems, and the other to the other system. The constituents are β, which is the compound Al_2Zn_3, probably containing a certain amount of copper in solution, and ϵ, which is probably a solution of zinc in the compound $CuZn_6$.

In order to show the method of formation of this eutectoidal complex, the alloy 9Z12 was slowly cooled from above the liquid, and quenched at 381° C. It was desired to obtain an alloy in which the primary separation consisted solely of the complex, and which also contained little or no ternary eutectic. It will be seen that 9Z12 is the alloy which comes nearest to this specification. Fig. 32 shows the microstructure of this alloy when slowly cooled from above the liquid, and quenched at 381° C. It will be seen that, as was to be expected, there is only a primary separation of the $\beta-\epsilon$ complex, together with a small quantity of chilled liquid.

In the alloys containing 3 per cent. of copper, no thermal evidence can be obtained for the existence of the binary complex, although the microstructure shows that it is present. The reason of this doubtless is that in this section the separation of the aluminium-zinc eutectic only just precedes that of the ternary eutectic, and the two reactions occur at so nearly the same temperature that they are not separated by the thermo-couple. In sections of the model representing alloys containing 4 per cent. of copper and upwards it is easily detected.

The ternary eutectic must now be discussed. The three phases composing it are obviously η, β, and ϵ, but the manner in which it is formed is not always the same. In the majority of cases it is formed as though it were a binary eutectic, one of whose constituents is the $\beta-\epsilon$ complex, and the other is η, which arises from the reaction between primary ϵ and the liquid. This can be seen well in fig. 37.

While the eutectic is generally formed as outlined above, this is not always the case. Over a small range of composition, between about 5 and 15 per cent. of aluminium, the copper-content varying between 2·5 and 4 per cent., the eutectic resembles in its method of formation a binary eutectic composed of the $\beta-\epsilon$ complex, and the complex consisting of the depressed $\eta-\beta$ eutectic, of the aluminium-zinc series. In a third case, the ternary eutectic is formed from this $\eta-\beta$ complex and ϵ.

The exact composition of the ternary eutectic has been determined mainly from the microstructure. A very small change in the composition makes a very great increase in the amount of eutectic present. This will be seen by comparing fig. 33 (alloy 3Z6) with fig. 35 (alloy 4Z6). In the former, there is only a small trace of ternary eutectic in the boundaries of the crystals; in the latter, a very large part of the alloy consists of this eutectic, the change being brought about by the addition of only 1 per cent. of copper. Similarly, considering figs. 35, 36, and 37 (alloys 4Z6, 4Z7, and 4Z8), in fig. 35 there are large crystals of primary ϵ and some evidence for primary η as well. Fig. 36 represents an alloy which must be very near the ternary eutectic composition, as there is no constituent present which can definitely be said to be a primary separation, while in fig. 37 it is fairly evident that the $\beta-\epsilon$ complex is the primary separation. It would appear from this that the ternary eutectic cannot be very far removed from the composition:—Cu 4 per cent., Al 7 per cent., Zn 89 per cent.

The occurrence of the ternary eutectic appears to be limited to a very small part of the system, and it is obvious that it is not the same eutectic as that referred to by Carpenter and Edwards. Indeed, the evidence suggests that, at the temperature at which it is formed, it does not exist over a much larger area than that with which the present investigation is concerned.

Before passing on to the consideration of the alloys containing 2 and 3 per cent. of copper, reference may be made to those sections of the model which are parallel to the base, *i.e.*, those which represent the condition of the alloys at constant temperatures. These are shown in figs. 19–21. Fig. 19 represents a horizontal section or plan cut through the model at 400° C.

The next plan (fig. 20) represents the constitution of the alloys at 300° C., while fig. 21 shows the constitution at 200° C. It is interesting to note that there is no difference between the phases present in the field below the ternary eutectic and in that below the area containing $\beta-\epsilon$ only. This is due to the fact that there is β in both regions, which decomposes into $\eta+\gamma$, and there is also ϵ in both regions, which passes through the transformation temperature unaltered. While there is no phase difference in the alloys below about 285° C. in that part of the diagram where three phases are present, there is a difference in the arrangement of these phases, for, below the ternary eutectic, there are two types of η present, one which has separated from the liquid, and one which has arisen as a result of the decomposition of β, while, in those alloys which contain no ternary eutectic, only the second kind of η is present.

Finally, fig. 18 is a contour map of the liquidus surface. The valleys of the $\eta - \beta$ and the $\beta - \epsilon$ complexes, meeting at the ternary eutectic, can be readily distinguished.

The sections containing 2 per cent. of copper and 3 per cent. of copper have not yet been considered in this paper. In this connection, reference must be made to figs. 22 and 23 or to the model. In figs. 22 and 23, the line BC separates those alloys whose primary crystallisation is η from those which commence by depositing ϵ from the liquid. It will be seen that the lines representing alloys containing 2 and 3 per cent. of copper cut this line, so that those alloys in these series lying to the right of BC have ϵ as a primary separation, while, in those to the left, η is the first separation. In the former case, the separation of ϵ is followed by the reaction $\epsilon +$ liquid $= \eta$, but, if the composition of the alloy is represented by a point lying within the shaded area, BCJ, of fig. 23, there is not enough ϵ to complete this reaction, and the result is that there is only $\eta +$ liquid left over. To the right of CJ we have $\eta + \epsilon +$ liquid.

In the case of the alloys with 2 per cent. of copper the reaction dies out very rapidly—probably on the addition of about 1 per cent. of aluminium, but in the alloys containing 3 per cent. of copper the reaction takes place over a much greater range of composition, ceasing at about 5 per cent. of aluminium. The evidence for the existence of this reaction is, perhaps, not very strong in the 2 per cent. copper series; all that can be said with certainty is that it exists in an alloy containing 98 per cent. of zinc and 2 per cent. of copper, but that the addition of quite a small amount of aluminium appears to eliminate it. In the case of the alloys containing 3 per cent. of copper, however, the evidence is much stronger. The reaction is indicated by the thermal curves of the alloys containing 2 per cent. of aluminium and probably also on those of 3Z4, and in alloys containing at least as much as 1·5 per cent. of aluminium, the microscope shows evidence of primary separation of ϵ.

In the alloys containing both 2 per cent. and 3 per cent. of copper there must be a very narrow area in which the $\beta - \eta$ complex solidifies, but there is this difference: that in the 2 per cent. series the lower boundary of the area represents the final solidification of this complex, while in the 3 per cent. series it is the line of solidification of the ternary eutectic. This will be seen more clearly when the sections representing alloys of constant aluminium-content are considered.

In the 3 per cent. copper series this area does not commence until about 5 per cent. aluminium is reached, as there is no separation of either primary η or β in the case of the alloys containing less than 5 per cent. of aluminium. The upper boundary of the area will meet the lower one at this composition, and also at a point (outside the diagram) which marks the limit of the separation of η. The lower limit of the area in the case of the 2 per cent. copper series is not well fixed, but it appears to be in the neighbourhood of 1 per cent. aluminium.

The lines separating the fields containing $\eta+$liquid from the fields containing $\eta+\epsilon+$liquid are shown dotted, as their exact position has not been determined.

The sectional diagrams representing alloys of constant aluminium-content are shown in figs. 10 to 17. Fig. 10, which represents the equilibrium conditions of the alloys of copper and zinc, has already been considered. The remaining sections can be divided into two groups: those containing up to 5 per cent of aluminium, where the primary separation at the zinc-rich end of the section consists of η, and those containing 7 per cent. of aluminium and over, where the primary separation consists of β. To make matters clearer, it will be well to consider a series of typical alloys in the sections containing, say, 2 per cent. of aluminium and 10 per cent. of aluminium. In the first of these sections (fig. 11) the alloy containing 1 per cent. of copper (1Z2) commences to solidify at about 407° C. by the separation of η, which continues until the temperature of about 380° C. is reached, when the binary complex of η and β commences to separate, this separation taking place over a range of about 2° C.

In the case of the alloy 6Z2 the first material to solidify is ϵ, the solidification commencing at 480° C. and continuing with falling temperature until the reaction $\epsilon+$liquid $=\eta$ commences at 400° C. At 378° C. the ternary eutectic separates.

The depressed binary complex is shown on a larger scale in the inset diagram of fig. 11. It is not possible to separate these lines pyrometrically, but theoretically they must exist. The lowering of the ternary eutectic, compared with that of the binary, appears to be about 2° C and is just perceptible on most, if not all, the sections.

Alloys 2Z10, 3Z10, and 5Z10 may be taken as typical of the second group (fig. 15). In the case of 2Z10 and 3Z10 the first constituent to separate on cooling is β, the crystallisation commencing at 415° C. and 400 C. respectively, but in the case of 5Z10 solidification commences at 400° C. by the separation of ϵ. The β continues to separate in 2Z10 until the temperature of 379° C. is reached, when the $\beta-\eta$ complex is deposited over a very narrow range of temperature. When 5 per cent. of copper is present, β separates from 400° C. to 390° C. and the $\beta-\epsilon$ complex comes out of solution during the next 12° C., after which the remaining liquid solidifies as ternary eutectic. The alloy containing 8 per cent. of copper behaves in the same way (at somewhat different temperatures) except that the primary separation is no longer β but ϵ.

There remains the small group of alloys lying between the two types of section where the primary zinc-rich separations are β and η respectively. These are represented by the diagram showing the section containing 6 per cent. of aluminium (fig. 13). Here it will be seen that, in alloys containing less than about 2·5 per cent. of copper the primary separation consists of crystals of β; at about 2·5 per cent. of copper it consists of the pure $\beta-\eta$ complex; and between about 2·5 of copper and 3·5 per cent. of copper it consists of η. Higher copper-contents give rise to a primary separation of ϵ. The temperature ranges over which these reactions occur are in general too small to be shown by the thermal curves, but an examination of the constitution of the alloys containing 6 per cent. of aluminium on the various constant copper sections shows that the diagram must be similar to that given in fig. 13. This can also be seen from fig. 18, on which the various binary complex valleys are plotted. It will be seen that the line representing the alloys containing 6 per cent. of aluminium starts in the field where the primary separation is β, then crosses the $\beta-\eta$ complex valley, enters the primary η field, and finally passes into the primary ϵ area. This part of the diagram is plotted on a larger scale in the inset to fig. 13.

Reference has been made in several places to the reaction,

$$\beta = \eta+\gamma.$$

This reaction, which was first observed by Rosenhain and Archbutt in the aluminium-zinc series, occurs in all the alloys containing more than about 1 per cent. of aluminium, *i.e.*, in all alloys in which β exists, either as a primary separation or as one constituent of an eutectic or a complex. It was found that, even with the slow rates of heating and cooling adopted, there was a lag of about 20° C. to 25° C. between the temperature of the reaction as indicated by the heating curves and by the cooling curves. The points given by the heating curves are very much more regular than those given by cooling curves, and this, together with the fact that there is much less liability for an arrest point to show superheating on a heating curve than to show undercooling on a cooling curve, has decided the authors to regard the temperature shown on the heating curves as the correct one, rather than to attempt to take a mean.

Perspective drawings of the model are given in figs. 22, 23 and 24. In each of these, various planes are shaded so as to emphasise the different stages in the solidification of the alloys, and above each drawing is a plan of the shaded areas. In fig. 22 the liquidus surfaces are shaded. In any alloy whose composition is indicated by a vertical line passing through the area ABCD, solidification commences by the separation of η. Similarly, over the area CDEFG, the primary separation is β, while ϵ commences to separate in the area CGHB. The point C represent the constitution of the ternary eutectic, while CD and CG are the *loci* of the separation of the $\eta-\beta$ and the $\beta-\epsilon$ complexes, free from any other primary separation.

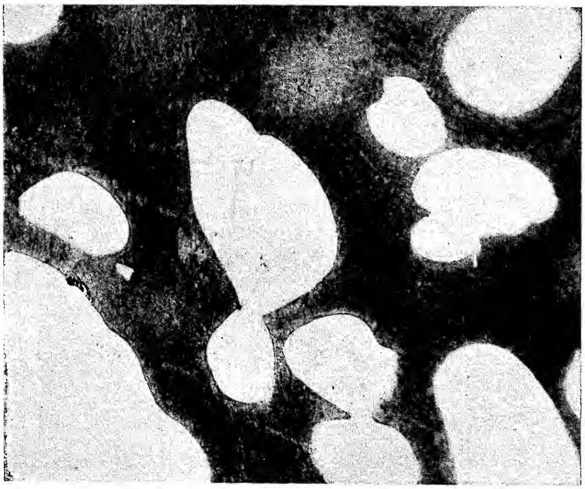
Fig. 23 represents the next stage in the solidification of the alloys. The $\eta-\beta$ complex commences to separate at a temperature indicated by the plane COPNM, the $\beta-\epsilon$ eutectic beginning to crystallise over the area CMLGK. The area CKIB marks the temperature at which η commences to solidify as a result of the reaction $\epsilon+\text{liquid} = \eta$. Fig. 24 represents the solidus surface of the system, which is divided into five areas which may be tabulated as below:—

No.	Area.	Description.
1	AJOP	End of solidification of η by itself.
2	JIQO	" " in presence of ϵ.
3	OPNU	" " of $\eta-\beta$ complex.
4	OUTRQ	The ternary eutectic plane.
5	RST	End of solidification of $\beta-\epsilon$ complex.

The area VWXY in fig. 22 indicates the temperature at which the decomposition of β takes place.

Afterword.

The authors wish to express how much they owe to Dr. W. Rosenhain, F.R.S., Superintendent of the Metallurgical Department of the Laboratory, for the interest he has shown in the work, for the manner in which he has always been willing to assist them with advice and suggestions, and especially for the advantages which they gained, both in the accuracy and in the expedition of the work, through using the apparatus and methods designed and installed in his Department of the National Physical Laboratory. To Mr. W. H. Withey, B.A., and Mr. P. G. Ward, B.Sc., A.R.C.S., of the Chemical Division, who carried out the majority of the analyses, and to others of their colleagues, they would express their indebtedness.



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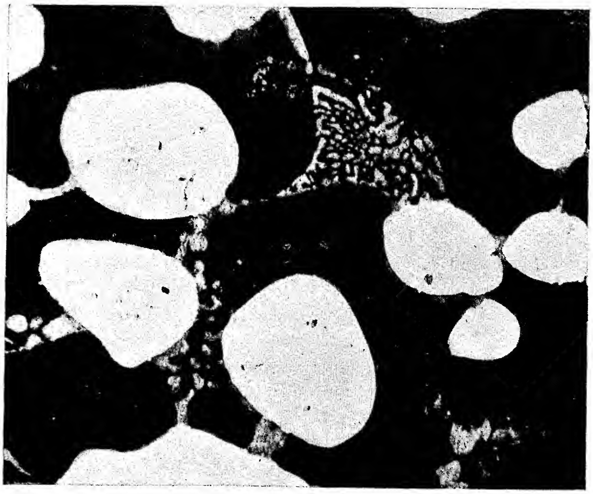

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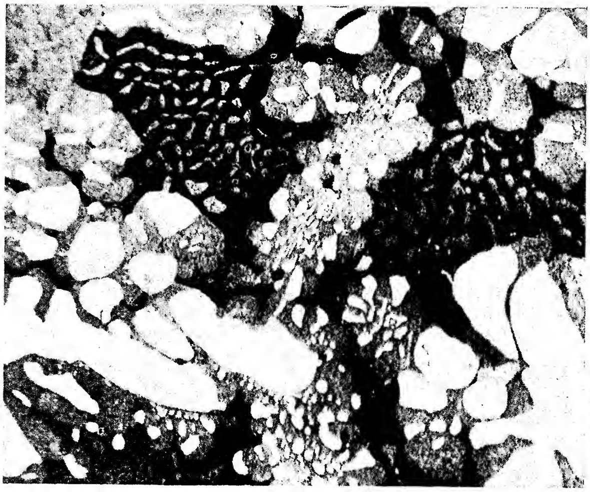

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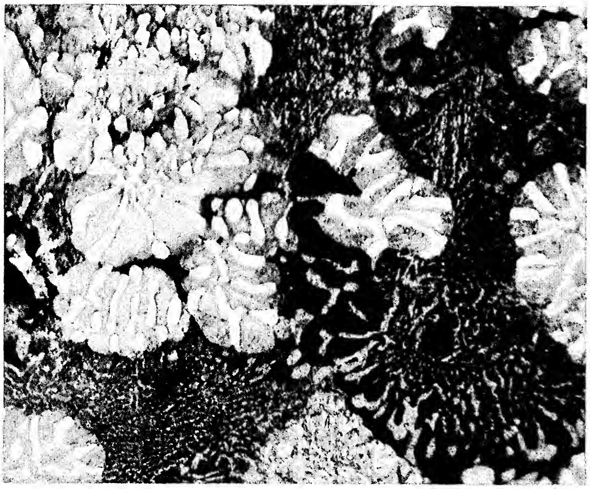

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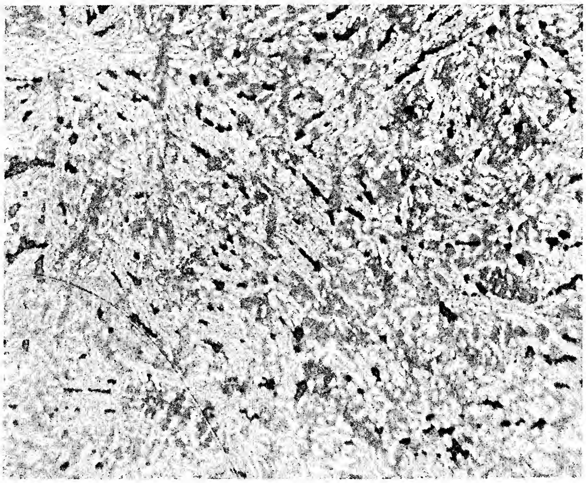

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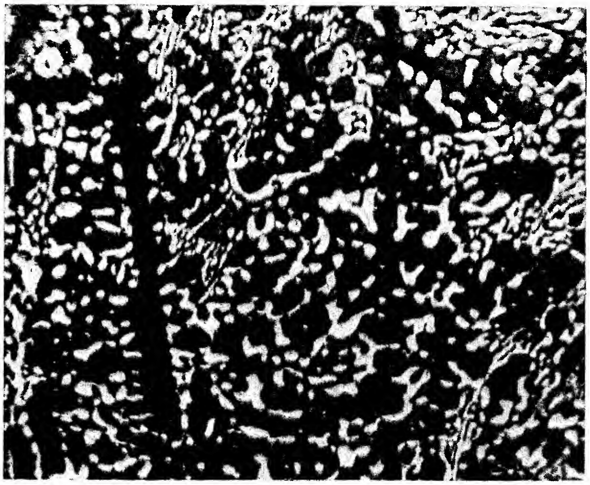

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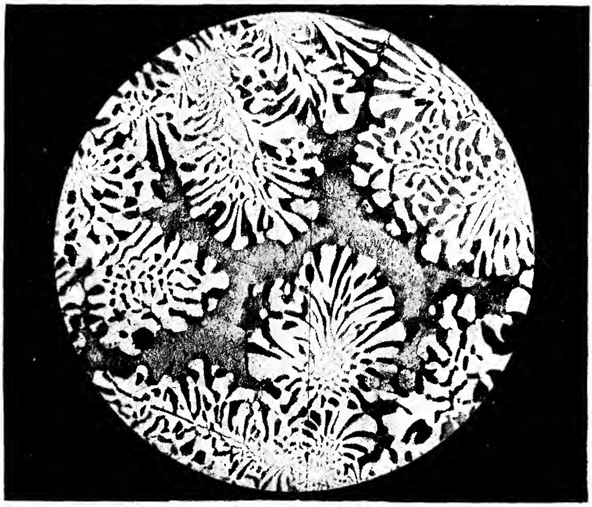

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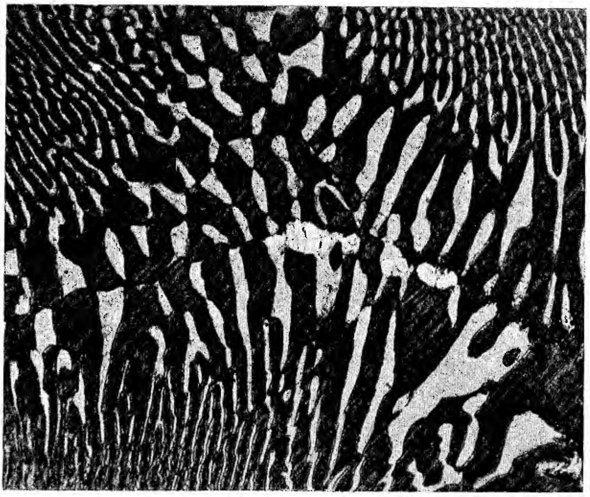

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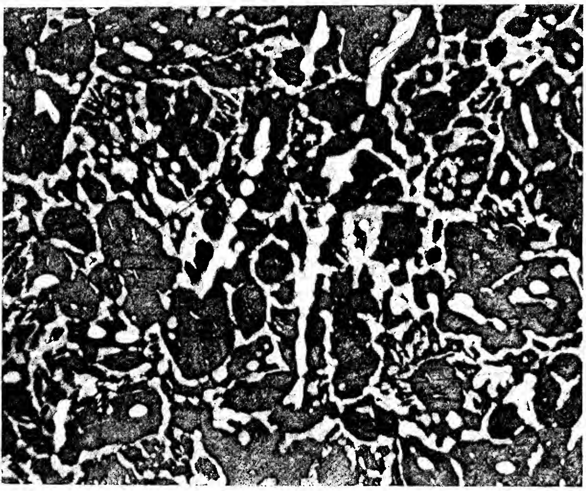

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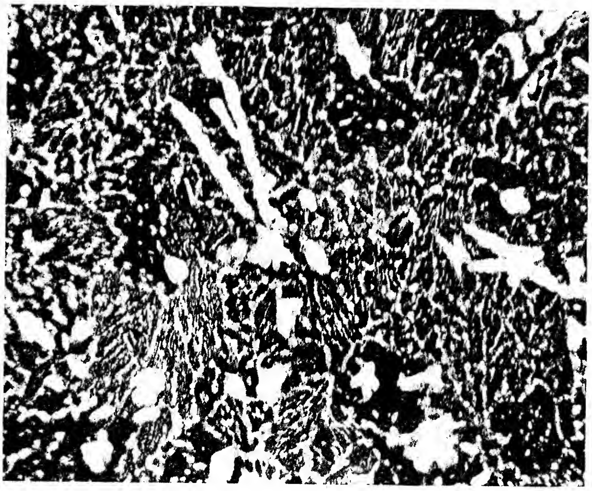

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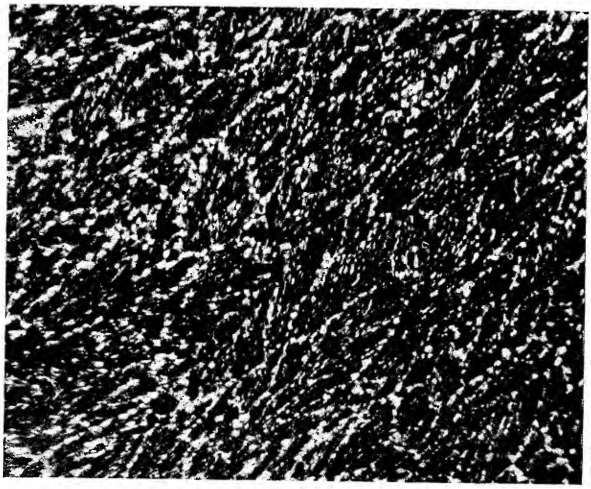

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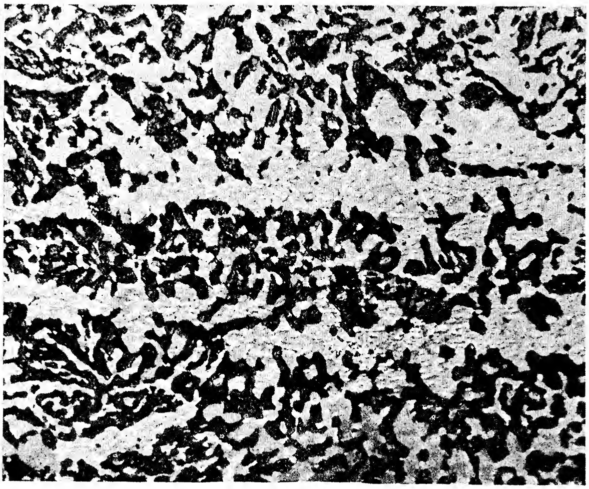

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DESCRIPTION OF PLATES.

PLATE 1.

Fig. 26.—7Z½. Slowly cooled from above the liquidus to 345° C. × 300.
Fig. 27.—7Z2. Slowly cooled from above the liquidus to 345° C. × 300.
Fig. 28.—7Z8. Slowly cooled from above the liquidus to 345° C. × 300.
Fig. 29.—7Z10½. Slowly cooled from above the liquidus to 350° C. × 300.
Fig. 30.—7Z12. Annealed at 345° C. × 300.
Fig. 31.—7Z15. Annealed at 345° C. × 300.

PLATE 2.

Fig. 32.—9Z12. Slowly cooled from above the liquidus to 350° C. × 100.
Fig. 33.—3Z6. Slowly cooled from above the liquidus to 370° C. × 300.
Fig. 34.—4Z4. Annealed at 300° C. × 300.
Fig. 35.—4Z6. Annealed at 300° C. × 300.
Fig. 36.—4Z7. Annealed at 300° C. × 300.
Fig. 37.—4Z8. Annealed at 300° C. × 300.

The Vacuum Arc Spectra of Sodium and Potassium.

By SNEHAMOY DATTA, M.Sc. (Calcutta), D.I.C., Research Student, Imperial College of Science.

(Communicated by Prof. A. Fowler, F.R.S.—Received February 15, 1921.)

1. *Introductory.*

In connection with the investigation of spectral series, the need for more accurate measurements of the spectra of the alkali metals has long been felt, especially in the case of the diffuse series and the higher members of the sharp series. When it was found that the "sodium vapour lamp," recently described by Lord Rayleigh,* gave extremely narrow bright lines, such that the term diffuse as applied to one of the series becomes a misnomer, it seemed possible that the desired improvement in the measures of the wave-lengths might be attained by the use of this ideal vacuum arc as a source. Definite improvements in the measures for sodium, as proved by the constancy of the separations of pairs of lines, suggested that a potassium vapour lamp might also be used with probable success. The potassium lamp was much more troublesome than the sodium one, and the lines of the diffuse series were less sharply defined. The new measures

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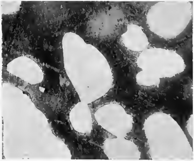
* R. J. Strutt, Bakerian Lecture, 'Roy. Soc. Proc.,' A, vol. 96, p. 272 (1919).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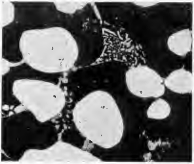
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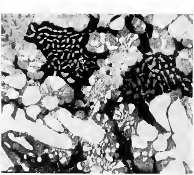
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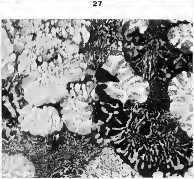
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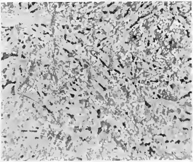
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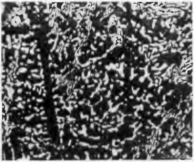
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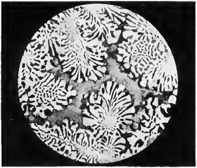

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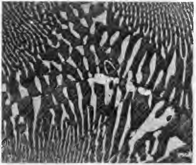

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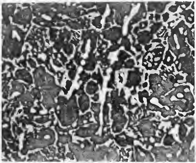

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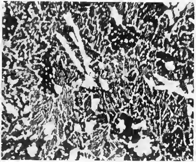

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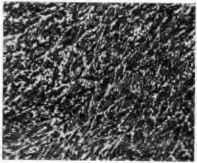

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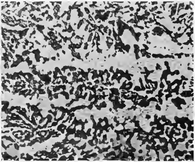

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PLATE 2.

Fig. 32.—9Z12. Slowly cooled from above the liquidus to 350° C. × 100.
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